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- (4) Lubricating oil composition.
- (a) A lubricating oil composition comprising a major amount of at least one lubricating base oil, from 0.05 to 5 % by weight of at least one zinc dithiophosphate, and from 0.01 to 10 % by weight of at least one unsaturated aliphatic alcohol of from 16 to 24 carbon atoms, the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate being from 0.1 to 10, has excellent thermostability and oxidation stability and has excellent effect in improving load carrying capacity and wear resistance.

### **LUBRICATING OIL COMPOSITION**

#### BACKGROUND OF THE INVENTION

### (a) Field of the Invention

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The present invention relates to a lubricating oil composition which can be suitably used as hydrautic fluid, traction fluid, bearing oil, gear oil, engine oil, etc.

## (b) Description of the Related Art

Zinc dithiophosphates have been widely used in lubricating oils having requirements for the function of improving wear resistance and load carrying capacity, thermostability, and oxidation stability.

Recently, as the service environment of these lubricating oils has become severe, there has arisen a demand particularly for lubricating oils having such high thermostability and oxidation stability as to withstand use at high temperature.

As a means of improving thermostability and oxidation stability, in Japanese Patent Application Kokai Koho (Laid-open) No. 60-248796 proposed is adding zinc dithiophosphates into lubricating base oils together with other additives including nitrogen-containing copolymers, metallic detergent-dispersants, ashless detergent-dispersants, etc. However, such additives decrease load carrying capacity and wear resistance and cannot bring about sufficient increase in thermostability and oxidation stability, and therefore, the obtained lubricating oil cannot be prevented sufficiently from formation of sludge and coloration and discoloration.

## SUMMARY OF THE INVENTION

The present invention has been made under the above-described circumstances, and the object of the present invention is to provide a lubricating oil composition which has not only excellent effect in improving load carrying capacity and wear resistance but also excellent thermostability and oxidation stability whereby formation of sludge and coloration and discoloration are inhibited and heat degradation and oxidation degradation can be retarded.

We have made study diligently for dissolving the above-described problems and have found that a lubricating oil composition satisfying the above-described object is obtainable by blending unsaturated aliphatic alcohols of from 16 to 24 carbon atoms together with zinc dithiophosphates into lubricating base oils in a specific ratio, and on the basis of the finding, we have eventually completed the present invention.

That is, the present invention provides a lubricating oil composition, comprising:

- (A) a major amount of at least one lubricating base oil;
- (B) from 0.05 to 5 % by weight of at least one zinc dithiophosphate having a structure represented by the following general formula (1)

wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> is independently a primary alkyl group of from 2 to 30 carbon atoms, a secondary alkyl group of from 3 to 30 carbon atoms, a cycloalkyl group of from 6 to 30 carbon atoms, an aryl group of from 6 to 14 carbon atoms or an alkylaryl group of from 7 to 30 carbon atoms; and

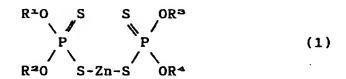
(C) from 0.01 to 10 % by weight of at least one unsaturated aliphatic alcohol of from 16 to 24 carbon

atoms, wherein the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate, (C)/(B), is from 0.1 to 10.

The oxidation stability of the lubricating oil composition of the present invention can be further improved by adding detergent-dispersants. That is, the present invention also provides a lubricating oil composition, comprising:

(A) a major amount of at least one lubricating base oil;

(B) from 0.05 to 5 % by weight of at least one zinc dithiophosphate having a structure represented by the following general formula (1)



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wherein R1, R2, R3, and R4 are as defined above;

(C) from 0.01 to 10 % by weight of at least one unsaturated aliphatic alcohol of from 16 to 24 carbon atoms; and

(D) a relatively small amount of at least one detergent-dispersant, wherein the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate, (C)/(B), is from 0.1 to 10.

The lubricating oil composition of the present invention can be suitably used as hydraulic fluid, traction fluid, bearing oil, gear oil, engine oil, etc. even in sever circumstances where exposure to high temperature is inevitable.

#### THE PREFERRED EMBODIMENTS OF THE INVENTION

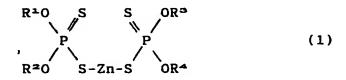
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The component (A), i.e. the lubricating base oil to be used in the lubricating oil composition of the present invention may be any one generally used in lubricating oils and is not particularly limited. Generally, a mineral oil or a synthetic oil each having a kinematic viscosity of from 5 to 10,000 cSt as measured at 40 °C may be used.

The mineral oil is not particularly limited so far as it satisfies the above-described condition, and some examples include those obtained by refining lubricating oil fraction of petroleum by means of solvent refining, hydrorefining, clay treatment, or a combination thereof and highly aromatic fractions obtained by solvent refining of lubricating oils, or hydrogenation products of the highly aromatic fractions. Some examples of the synthetic oil include alkyl-substituted aromatic compounds, poly- $\alpha$ -olefin oils, ester oils, diester oils, hindered ester oils, synthetic naphthene oils, polyglycol oils, and mixtures thereof.

The zinc dithiophosphate (ZnDTP) to be used as the component (B) in the lubricating oil composition of the present invention is the compound represented by the following general formula (I)



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wherein each of R¹, R², R³, and R⁴ is independently a primary alkyl group of from 2 to 30 carbon atoms, preferably from 3 to 12 carbon atoms, a secondary alkyl group of from 3 to 30 carbon atoms, preferably from 3 to 12 carbon atoms, a cycloalkyl group of from 6 to 30 carbon atoms, an aryl group of from 6 to 14 carbon atoms or an alkylaryl group of from 7 to 30 carbon atoms, preferably from 9 to 24 carbon atoms.

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Some examples of the zinc dithiophosphate include zinc dialkyldithiophosphates, such as zinc di-n-propyldithiophosphate, zinc diisopropyldithiophosphate, zinc di-n-butyldithiophosphate,

zinc diisobutyldithiophosphate,
zinc di-sec-butyldithiophosphate,
zinc di-n-amyldithiophosphate,
zinc diisoamyldithiophosphate,
zinc di-h-hexyldithiophosphate,
zinc di-sec-hexyldithiophosphate,
zinc di-sec-hexyldithiophosphate,
zinc bis(2-ethylhexyl)dithiophosphate,
and
zinc didecyldithiophosphate,
zinc diaryldithiophosphates, such as
zinc diphenyldithiophosphates, and
zinc bis(alkylaryl)dithiophosphates, such as
zinc bis(octylphenyl)dithiophosphates,
zinc bis(dodecylphenyl)dithiophosphates,
zinc bis(dodecylphenyl)dithiophosphates.

The above-described component (B) i.e. the zinc dithiophosphate is present in the lubricating oil composition of the present invention at a concentration of from 0.05 to 5.0 % by weight, preferably from 0.1 to 3.0 % by weight. If the percentage of the component (B) is less than 0.05 % by weight of the lubricating oil composition, the effect of improving wear resistance and load carrying capacity will be small. On the other hand, even if the percentage of the component (B) exceeds 5.0 % by weight of the lubricating oil composition, larger effect cannot be expected.

The unsaturated aliphatic alcohol of from 16 to 24 carbon atoms which is to be used as the component (C) in the lubricating oil composition of the present invention may be any alcohol having the above-described number of carbon atoms and at least one double bond in each molecule. The preferred are alcohols having an iodine number of about not less than 50. Some examples of the preferred unsaturated aliphatic alcohols include cis-11-hexadecene-1-ol (C<sub>16</sub>H<sub>32</sub>O), cis-9-octadecene-1-ol (oleyl alcohol, C<sub>18</sub>H<sub>36</sub>O), 3,7,11,15-tetramethyl-2-hexadecene-1-ol (C<sub>20</sub>H<sub>40</sub>O), 9-eicosene-1-ol (C<sub>20</sub>H<sub>40</sub>O), 11-docosene-1-ol (C<sub>22</sub>H<sub>44</sub>O), 13-docosene-1-ol (C<sub>22</sub>H<sub>44</sub>O), 12-tetracosene-1-ol (C<sub>24</sub>H<sub>48</sub>O), and 13-tetracosene-1-ol (C<sub>24</sub>H<sub>48</sub>O).

Among these, the particularly preferred examples include 11-docosene-1-ol, 13-docosene-1-ol, 9-eicosene-1-ol, and cis-9-octadecene-1-ol (oley) alcohol).

The above-described component (C), i.e. the unsaturated aliphatic alcohol is present in the lubricating oil composition of the present invention at a concentration of from 0.01 to 10 % by weight, preferably from 0.05 to 6.0 % by weight, and the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate, (C)/(B) is from 0.1 to 10, preferably from 0.2 to 3.0. If the percentage of the component (C) in the lubricating oil composition is less than 0.01 % by weight or (C)/(B) is less than 0.1, the component (C) cannot produce much effect of inhibiting the formation of sludge. On the other hand, even if the percentage of the component (C) exceeds 10 % by weight or (C)/(B) exceeds 3.0, larger effect cannot be expected.

The oxidation stability of the lubricating oil composition of the present invention comprising the above-described lubricating base oil (A), the component (B), and the component (C), can be further improved by adding a relatively small amount of at least one detergent-dispersant (component D).

The detergent-dispersant to be used in the present invention may be any known detergent-dispersant, and some examples include metallic detergent-dispersants such as petroleum sulfonates, phosphonates, and phenates, and ashless detergent-dispersants, such as succinic acid derivatives and amine-type detergent-dispersants. Some typical examples of the detergent-dispersants which may be suitably used are Ca sulfonate and Ca phenate. The component (D), i.e. the detergent-dispersant is present in the lubricating oil composition of the present invention preferably at a concentration of from 0.01 to 5.0 % by weight, more preferably from 0.1 to 1.5 % by weight, furthermore preferably from 0.2 to 1.0 % by weight.

The above-described lubricating oil composition of the present invention comprising the lubricating base oil (A), component (B), and component (C) or the lubricating base oil (A), component (B) component (C) and component (D) may further contain a relatively small amount of at least one additive compound (component E) selected from the group consisting of phosphoric esters, phosphorous esters, amine salts of phosphorous esters, and amine salts of phosphorous esters.

Some examples of the phosphoric esters and the phosphorous esters which of the be suitably used are the compounds represented by the following general formulas (II) and (III) respectively:

$$R=0$$
 $R=0$ 
 $P=0$  (II) and  $R=0$ 
 $R=0$ 
 $R=0$ 

wherein each of R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, and R<sup>10</sup> is, for example, independently a hydrogen atom, an alkyl group of from 4 to 30 carbon atoms, an aryl group of from 6 to 30 carbon atoms, or an alkylaryl group of from 7 to 30 carbon atoms, and two or more of them may be identical with each other or they may be different from each other.

Some typical examples of the phosphoric esters and the phosphorous esters include triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, tris(isopropylphenyl)phosphate, butyl acid phosphate, 2-ethylhexyl acid phosphate, lauryl acid phosphate, oleyl acid phosphate, stearyl acid phosphate, dibutyl hydrogen phosphite, dioctyl hydrogen phosphite, and distearyl hydrogen phosphite.

Some examples of the amine salts of phosphoric esters and the amine esters of phosphorous esters include lauryl amine salt, oleyl amine salt, coconut amine salt, and beef tallow amine salt.

The component (E), i.e. the additive compound is present in the lubricating oil composition of the present invention preferably at a concentration of from 0.01 to 5.0 % by weight, more preferably from 0.1 to 1.5 % by weight, furthermore preferably from 0.2 to 1.0 % by weight. Addition of the component (E) improves wear resistance still more.

Further, the lubricating oil composition of the present invention may contain other additives which has been generally added into lubricating oils, for example, antioxidants, viscosity index improvers, corrosion inhibitors, rust-preventive agents, metal deactivators, or antifoaming agents.

The following Examples are given to illustrate the present invention in more detail. The scope of the invention is not, however, meant to be limited to the specific details of these Examples.

## EXAMPLES 1 TO 14 AND COMPARATIVE EXAMPLES 1 TO 5

Table 1 shows the composition and the test results of the lubricating oil compositions of the Examples and Comparative Examples.

The tests made in the Examples and Comparative Examples were carried out by means of the following methods.

## (1) Coloration and Discoloration, (2) Property of Inhibiting Formation of Sludge

These properties were examined according to JIS K 2540, Method of Testing the Thermostability of Lubricating Oils, at a testing temperature (oil temperature) of 140 °C. The catalysts used were copper wire, iron wire, and aluminum wire each being \$\phi\$ 1.6 mm \$\times\$ 8 cm.

Evaluation of the coloration and discoloration (1) was carried out by removing the sample used every 24 hour to observe the color of the sample (ASTM JIS K 2580) and is shown as the time (h) required of the color to exceed the ASTM color grade 4. Evaluation of the property of inhibiting formation of sludge was carried out by observing the above-described sample and was shown as the time (h) required of the deposition of separated material to be observed.

### (3) Oxidation Stability

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Oxidation stability was examined according to JIS K 2514, paragraph 3.1, Method of Testing the Oxidation Stability of Lubricating Oils for Internal Combustion Engines (so called ISOT).

Conditions of ISOT

The condition for the samples from Example 2 and Comparative Example 1 were @165.5  $^{\circ}$ C  $\times$  24 h, and the condition for the sample from Example 12 was @150  $^{\circ}$ C  $\times$  96 h.

# (4) Wear Resistance (Falex wear resistance)

The examination of wear resistance was conducted according to ASTM-D 2670.

10	Materials	block	SUJ-2 (Rc62)
		pin	SKH-1 (Rc65)

The marks shown in Table 1 have the following meaning

1: 150 neutral oil (produced by Idemitsu Kosan Co., Ltd.)

2: DOA (Trade-name, dioctyl adipate produced by Nippon Cooper Company)

3: fatty acid esters of trimethylolpropane (Trade-name: Unistar H312R produced by NIPPON OIL & FATS CO., LTD.)

\*4: 1,2-bis(methylcyclohexyl)-2-methylpropane

\*5 : zinc di-sec-hexyldithiophosphate (Trade-name: LZ677A, produced by Lubrizol Corporation)

\*6: a mixture of zinc di-(C<sub>4</sub>-C<sub>6</sub>)-alkyldithiophosphates (Trade-name: OLOA267, produced by Chevron Chemical Company)

7 : zinc bis(alkylaryl)dithiophosphate (Trade-name: OLOA260, produced by Chevron Chemical Com-

\*8 : oleyl alcohol (cis-9-octadecene-1-ol) (produced by Kyowa Yushi Co., Ltd.)

9:85TBN Ca sulfonate + 150TBN Ca phenate (1:1 in weight ratio)

10:300TBN Ca sulfonate + 150TBN Ca phenate (1:2 in weight ratio)

\*11 : TCP (tricresyl phosphate) (Trade-name, produced by KYOWA HAKKO KOGYO CO., LTD.)

\*12 : polymethacrylate (number average molecular weight: 60,000) (produced by SANYO CHEMICAL INDUSTRIES, LTD.)

\*13 : silicone oil

\*14: Kalcohol 20 (Trade-name, produced by Kao Corp.)

\*15 : oleyi oleate (produced by Yuka Sangyo)

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1 *3 1 *3 ne oil *4  ant ***  ant ***  (0.5 ***  (1.7  (29.3)  (2.7  (30.5)  (30.7  (4.7  (4.7  (4.7  (5.7  (6.7  (7.7  (7.7  (9.7  (7.7  (9.7	25	20	15	- 10	5
#ineral oil *! dies ter oil ** hindered ester oil ** hindered ester oil ** hindered ester oil ** hindered ester oil ** sec-alkylZamp ** alkylzamp ** alkylzamp ** alkylzamp ** alkylaryldZamp **  3.4ocosene-1-oil oleyl alcohol ** detergent-dispersant ** chetergent-dispersant **  detergent-dispersant **  detergent-detergent-dispersant **  detergent-detergent-dispersant **  detergent-detergent-dispersant **  detergent-detergent-detergent **  detergent-detergent **  detergent-detergent **  detergent-detergent **  detergent-detergent **  detergent-detergent **  detergent			-	- 1	
#ineral oil *! dies tor oil ** hindered ester oil ** hindered ester oil ** hindered ester oil ** synthetic naphthene oil ** sec-alkylZafff ** alkylzafff ** alkylzafff ** alkylzafff **  13-docosene-1-oil oleyl alcohol **  detergent-dispersant *** detergent-dispersant ***  antifosming agent *** lauryl alcohol *** s viscosity index improver **!*  lauryl alcohol *** oleyl oleate **!*  and Discoloration (h) lauryl alcohol *** oleyl oleate **!*  and Discoloration (h) if inhibiting formation of sludge (h) if inhibiting formation of sludge (h) if inhibiting formation of sludge (h) if ovalue (mgKMI/g) id value (mgKMI/g) id value (mgKMI/g) id value (mgKMI/g) id value (mgKMI/g) in thericating oil composition (ppm) at in lubricating oil composition (ppm) at in lubrica		Example			
mineral oil *** diester oil *** hindered ester oil *** sec-alkylZamp ** alkylZamp ***  13-docosene-1-oi oleyl alcohol *** detergent-dispersant *** detergent-dispersant *** cletargent-dispersant *** antifoaming agent *** lauryl alcohol *** antifoaming agent *** antifoaming agent *** i and Discolaration (b) 120 < 192 < 24 if inhibiting formation of sludge (b) 120 < 192 < 24 if inhibiting formation of sludge (b) 120 < 192 < 24 stability (ISM) sest oil) cest oil) cest oil di value (mg/GH/g) cest oil) cest oil sid value (mg/GH/g) cest oil) cest oil centraling oil composition (prm) at in lubricating oil compositing (provided provided provided provided provided provided provided p		4	5	9	7
(C) 13-docosene-1-ol 0.2 0.5  (C) 13-docosene-1-ol 0.2 0.5  (C) 13-docosene-1-ol 0.2 0.5  (D) detergent-dispersant ***  (B) phosphoric ester ****  (B) phosphoric ester ****  (C) 13-docosene-1-ol 0.2 0.5  (D) detergent-dispersant ***  (E) phosphoric ester ****  (E) phosphoric ester ****  (E) phosphoric ester ****  (I) to switfosming agent ****  (E) phosphoric ester ****  (I) phosphoric ester ****  (E) phosphoric ester ****  (E) phosphoric ester ****  (I) phosphoric ester ***  (I) phosphoric ester ****		98.0	0.08	98.5	97.7
(C) 13-docosene-1-ol oley! alcohol ***  (D) datergent-dispersant ***  (E) phosphoric ester **!  (E) phosphoric ester **!  Itives viscosity index improver **!*  Itives viscosity index improver **!  Itives viscosity index improver **!  Itives viscosity index **!  Itives viscosity index improver **!  Iti		0.5	0.5	1.0	1.8
(B) detergent-dispersant ***  (B) phosphoric ester ***  (B) phosphoric ester ***  (C) though or an information of sludge (h) 120 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 192 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 193 < 1		0.5	0.5	0.5	0.5
phosphoric ester *!!  viscosity index improver *!:  lauryl alcohol *!* oleyl oleate *!!  Inhibiting formation of sludge (h) 120 < 192 < 192 < 192 (str. 40°C)  inhibiting formation of sludge (h) 120   192 (str. 40°C)  it value (wgKOH/g)   0.67/0.63   0.67/0.63   0.67/0.65   0.67/0.6					
viscosity index improver "!"  lauryl alcohol "!" oleyl oleate "!s inhibiting formation of sludge (h) 120 < 192 < 192 < 192 (cSt 40°C) st oil) st oil) st oil) st oil) f matters insoluble in n-pentane (wt%) (which is in lubricating oil composition (ppm) (wtw.) (which is in lubricating oil composition (ppm) (wtw.) (wtw					
lauryl alcohol ***  Coloration and Discoloration (h) 120 < 192 < 192 < 192   Property of inhibiting formation of sludge (h) 120   192   Oxidation stability (ISM)   192   Oxidation stability (ISM)   120   192   Oxidation visit (ISM)   192   Oxidation stability (ISM)   120   Oxidation st	-				
Coloration and Discolaration (h) 120 < 192 < Property of inhibiting formation of sludge (h) 120   192   192    Oxidation stability (ISMT)			•		
total acid value (wegkNH/g)  color (ASTNO  content of matters insoluble in n-pentane (wtx)  Za content in lubricating oil composition (ppm)  Falax abrasion resistance (wg)  427/40  427/40	31,8	<del>2</del> 23	<b>*</b>	> 088	<u>88</u>
Palex abrasion resistance (wg) 400°s × 60 min, block	333 <del>9</del>				
pin lig	<u>88</u>	316			
		(Continued o	(Continued on the following page)	ing page)	

55	50	45	40	35	30	25	20	15	10	5
		Table 1	Table 1 (Continued from the previous page)	on the pro	elous page)		-		•	
							Вхакріе			
				8	6	10	11	12	13	Z
Component (A) Cubricating base oil)		mineral oil *! diester oil ** hindered ester oil ** synthetic naphthene oil		98.0	99.0	0.08	8.96	92.0	0.98	89.0
Component (B)		sec-alkyiZnfff *6 p-alkyiZafff *6 alkyiaryiAZnfff *7		0.5	0.5	0.5	0.5	0.5	0.5	0.5
Component (C)		13-docesene-1-ol oleyl alcohol		0.5	0.5	0.5	0.5	0.5	0.5	0.5
Component (II)		detergent-dispersant detergent-dispersant	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0				0.2	0.5		
Component (E)		phosphoric ester ***						0.5		
Other additives		viscosity index improver antifoaming agent	VBT *12				2.0	6.0 0.001		
		lauryl alcohol *''* oleyl oleate *''s								
Coloration Oxidation	of in	Coloration and Discoloration (h) Property of inhibiting formation of sludge (h) (hidation stability (ISOT)	f sludge (h)	× 88	* ************************************	\$ <del>8</del>	<b>66</b> 55	200	\$25 \$25	216 216
viscosi total a color (	t of test	UNEW OIL/ LEST OIL) viscosity (CSt 40°C) total acid value (mgKOH/g) color (ASTM) content of matters insoluble in n Zn content in lubricating oil com	n-pentane (wt2) sposition (ppm)					25.227.2 0.75/0.62 10.5/12.5 476/457		
(4) Palex abr	투× 항영	Palex abrasion resistance (mg) 400 <sup>tms</sup> × 60 min, block pin					<u>ಹ</u> ್ಣ	80		
							(Continued or	(Continued on the following page)	(eged g	

3	Table 1 (Continued from the previous page)	ed fro	the previou	s page)			
8							
8				<b>ರ</b>	Comparative Example	xample	
			-	8	3	4	လ
8	*: ** ter oil ** aphthene oil **		99.5	99.5	99.5	93.0	98.0
8	np +5 onp +7		0.5	0.5	0.5	0.5	0.5
8	1-ol 1 **						-
Component (E) phosphoric es Other additives viscosity in	spersant ** spersant ***				· · <del>·</del>		
	ster *!!						
· Oute mark training	Viscosity index improver *13 antifoaming agent *13						
lauryl alcohol *14	ol *14   *18					0.5	0.5
Coloration and Discoloration (h) Property of inhibiting formation of sludge (h) Oxidation stability (ISOT) (new oil/test oil) viscosity (cSt 40°C) total scid value (mgKOH/g) color (ASTM) content of matters insoluble in n-pentane (w.Z. content in lubricating oil composition (p) Ralex abrasion resistance (mg)	ion (h)  restion of sludge ( )  /g)  Iuble in n-pentane ng oil composition block oin	(a) (w) (ppm)	24 < 24 < 0.67/1.84	^ ন্নন	* ಷಷ	× ন্তুন	<b>র</b> র

Table 1 shows that the addition of the component (C) such as 13-docosene-1-ol and oleyl alcohol, i.e., in particular, unsaturated aliphatic alcohols of from 18 to 22 carbon atoms improved thermostability and oxidation stability, and particularly, the properties of inhibiting coloration, discoloration, and formation of sludge were remarkably improved. As apparent from Comparative Examples 4 and 5, the compounds other than the components of the present invention could not produce the directed effects.

Claims

### 1. A lubricating oil composition, comprising:

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- (A) a major amount of at least one lubricating base oil;
- (B) from 0.05 to 5 % by weight of at least one zinc dithiophosphate having a structure represented by the following general formula (1)

$$R^{2}O$$
 S S  $OR^{3}$   
 $P$   $P$  (1)  
 $R^{2}O$  S- $Zn$ -S  $OR^{4}$ 

wherein each of R1, R2, R3, and R4 is independently a primary alkyl group of from 2 to 30 carbon atoms, a secondary alkyl group of from 3 to 30 carbon atoms, a cycloalkyl group of from 6 to 30 carbon atoms, an aryl group of from 6 to 14 carbon atoms or an alkylaryl group of from 7 to 30 carbon atoms; and

- (C) from 0.01 to 10 % by weight of at least one unsaturated aliphatic alcohol of from 16 to 24 carbon atoms, wherein the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate, (C)/(B), is from 0.1 to 10.
- 2. A lubricating oil composition, comprising:
  - (A) a major amount of at least one lubricating base oil;
  - (B) from 0.05 to 5 % by weight of at least one zinc dithiophosphate having a structure represented by the following general formula (1)

wherein each of R1, R2, R3, and R4 is independently a primary alkyl group of from 2 to 30 carbon atoms, a secondary alkyl group of from 3 to 30 carbon atoms, a cycloalkyl group of from 6 to 30 carbon atoms, an aryl group of from 6 to 14 carbon atoms or an alkylaryl group of from 7 to 30 carbon atoms;

- (C) from 0.01 to 10 % by weight of at least one unsaturated aliphatic alcohol of from 16 to 24 carbon atoms; and
- (D) a relatively small amount of at least one detergent-dispersant,
- wherein the weight ratio of the unsaturated aliphatic alcohol to the zinc dithiophosphate, (C)/(B) is from
- 3. The lubricating oil composition as claimed in claim 2, wherein the detergent-dispersant is present within the lubricating oil composition at a concentration of from 0.01 to 5.0 % by weight.
- 4. The lubricating oil composition as claimed in any of the claims 1 to 3, wherein the lubricating base oil is a mineral oil having a kinematic viscosity of from 5 to 10,000 cSt as measured at 40 °C or a synthetic oil having a kinematic viscosity of from 5 to 10,000 cSt as measured at 40°C.
- 5. The lubricating oil composition as claimed in any of the claims 1 to 4, wherein the zinc dithiophosphate is selected from the group consisting of zinc di-primary-(C3-C12)-alkyldithiophosphates, zinc-di-secondary-(C3-C12)-alkyldithiophosphates, zinc-di-se  $C_1$ )-alkyidithiophosphates, and zinc-bis- $(C_9$ - $C_{24}$ )-(alkylaryl)dithiophosphates.
- 6. The lubricating oil composition as claimed in any of the claims 1 to 5, wherein the unsaturated aliphatic alcohol is 11-docosene-1-ol, 13-docosene-1-ol, 9-eicosene-1-ol or cis-9-octadecene-1-ol.
- 7. The lubricating oil composition as claimed in claim 1 or 6, wherein the unsaturated aliphatic alcohol is 13docosene-1-ol or cis-9-octadecene-1-ol.
- 8. The lubricating oil composition as claimed in claim 1, wherein the lubricating base oil is a mineral oil, the zinc dithiophosphate is a mixture of zinc di-primary- ( $C_4$ - $C_6$ )-alkyldithiophosphates, and the unsaturated aliphatic alcohol is cis-9-octadecene-1-ol.
- 9. The lubricating oil composition as claimed in any of the claims 1 to 8, further comprising (E) a relatively small amount of at least one additive compound selected from the group consisting of phosphoric esters, phosphorous esters, amine salts of phosphoric esters, and amine salts of phosphorous esters.

- 10. The lubricating oil composition as claimed in claim 9, wherein the additive compound is present within the lubricating oil composition at a concentration of from 0.01 to 5.0 % by weight.
- 11. The lubricating oil composition as claimed in claim 2 or 3, wherein the unsaturated aliphatic alcohol is 13-docosene-1-ol.
- 12. The lubricating oil composition as claimed in claim 2 or 3, wherein the lubricating base oil is a mineral oil, the zinc dithiophosphate is a mixture of zinc di-primary-(C<sub>4</sub>-C<sub>6</sub>)-alkyldithiophosphates, the unsaturated aliphatic alcohol is 13-docosene-1-ol, and the detergent-dispersant is a mixture of Ca sulfonate and Ca phenate.
- 13. The lubricating oil composition as claimed in claim 2 or 3, wherein the lubricating base oil is a mineral oil, the zinc dithiophosphate is a mixture of zinc di-primary-(C<sub>4</sub>-C<sub>6</sub>)-alkyldithiophosphates the unsaturated aliphatic alcohol is 13-docosene-1-ol the detergent-dispersant is a mixture of Ca sulfonate and Ca phenate, and the additive compound is tricresyl phosphate.



# EUROPEAN SEARCH REPORT

EP 90 11 3167

	OCUMENTS CONSIDE			vant	CLASSIFICATION OF THE
egory	Citation of document with in of relevant	dication, where appropriate, passages		takn	APPLICATION (Int. CI.5)
x	DE-A-1 956 638 (SHELL)		1-4,6	6,7,9,	C 10 M 141/10 //
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-	* Cl.; page 1 - page 5, line 14,	page 6, mes o-11, page	, ,	1	C 10 M 129:06
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.,	US-A-2 945 810 (WALKER)		1-7	l l	C 10 N 40:00
Y				l	C 10 N 40:02
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.Υ	US-A-2 418 894 (McNAB et a	al.)	1-7		C 10 N 40:25)
	* Column 9, lines 20-74 *		1		
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	EP-A-0 286 996 (IDEMITSU	KOSAN)	1-4.	6,7,9.	
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	page 4, line 31 *				
			1	670	
Y	EP-A-0 291 006 (IDEMITSU	KOSAN)		,6,7,9,	
	* Cl.; columns 4,5 *		10		TECHNICAL FIELDS SEARCHED (Int. CI.5)
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Υ	EP-A-0 280 260 (IDEMITSU	KOSAN)	1-4	,6,7,9,	C 10 M
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	document of the same catagory		S. Woodmen		
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	A: technological background O: non-written disclosure		&: member of		ne patent family, corresponding